Reaction of Diphenyl Disulfide with Alkynes Promoted by Di-*tert*-butyl and Dibenzoyl Peroxide: a Useful Synthetic Route to 3- (and 2,3-) Substituted Benzo[*b*]thiophenes

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Thermal reactions of diphenyl disulfide 1 with phenylacetylenes 2a–e promoted by di-*tert*-butyl peroxide (TBP) at 110 or 150 °C provides a useful synthetic route to the (2-substituted) 3-phenylbenzo[*b*]thiophenes 4a–e, which result from intramolecular cyclization of 1-phenyl-2-(phenylthio)vinyl radical intermediates 3a–e. Similar reactions of the disulfide 1 with *tert*-butyl-and trimethylsilyl-acetylenes 2f and 2g also provide the corresponding benzothiophenes 4f and 4g in satisfactory yields; low yields of the benzothiophene products 4h, i, however, are obtained with hex-1-yne 1h and hex-3-yne 1i. Evidence is presented that the thermal reaction of the disulfide 1 with the alkynes 2 at 100 °C in the presence of dibenzoyl peroxide, while being of little use for the synthesis of benzothiophenes 4, generally leads to the 2-(phenylthio)vinyl benzoates 10; this is ascribed to initial addition of benzoyloxy radicals to alkyne triple bonds.

We have recently reported[1] that the reaction of diphenyl disulfide 1 with alkynes 2 promoted by phenyl radicals (produced by aprotic diazotization of aniline with pentyl nitrite) leads to 2-(phenylthio)vinyl radicals 3; such reactions proceed by addition of benzenethiyl radicals to carbon–carbon triple bonds. The vinylic radicals 3 underwent either homolytic intramolecular cyclization to the benzothiophenes 4 and/or an S_H2 reaction with the disulfide present to give 1,2-bis(phenylthio)ethylene adducts 5; the extent of each reaction was strongly dependent upon structural features and the bulkiness of adjacent R^1 substituents. Thus linear sp-hybridized 1-phenyl (and 1-*tert*-butyl) radicals 3 ($R^2 = Ph, Bu^t$) afforded benzo[*b*]-thiophene products 4 in low to moderate yields, whereas the bent sp^2-hybridized 1-alkylvinylic compounds 3 ($R^2 = $ alkyl) only gave bis sulfide adducts 5, provided that the R^1 substituent was small (H, Me). These results appeared of interest to us, particularly in that they disclosed a new attractive (though apparently limited) synthetic route to mono- and di-substituted benzothiophenes 4. In fact, although several methods have been reported for the synthesis of benzothiophenes substituted in the five-membered ring,[2] the synthetic potential of the intramolecular cyclization of 2-(phenylthio)vinyl radicals 3 remains virtually unexplored. Formation of benzothiophenes has been recently shown to occur in the thermal free-radical reactions of benzenethiol or diphenyl disulfide with acetylene, phenylacetylene, and prop-2-yn-1-ol.[3] However, such benzothiophene formation has been reported to occur in low yield and under very severe thermal conditions (590–600 °C). We were, therefore, prompted to further investigate the free radical reaction of diphenyl disulfide with a number of mono- and di-substituted phenyl- and alkyl-acetylenes, as well as with trimethylsilylacetylene, under a variety of conditions. Our primary aim was to uncover a new practicable, useful procedure for the preparation of benzothiophenes 4. Here we report the results of our study of the thermal reactions of the disulfide 1 with the alkynes 2 at 110 and 150 °C in the presence of di-*tert*-butyl peroxide (TBP) and/or at 100 °C in the presence of dibenzoyl peroxide (DBP).

Results and Discussion

A benzene solution of diphenyl disulfide 1 (0.1 mol dm³) containing 1 mol equiv. of the appropriate alkyne 2a–i was allowed to react, in the presence of a two-fold excess of TBP, in a sealed tube at 150 °C for 3 h, after which time GLC and GLC–MS analyses of the resulting reaction mixture generally showed that the disulfide 1 had been largely consumed, thioanisole (PhSMe) having been formed as the main reaction product (Table 1, column A). After removal of thioanisole and the excess of unchanged alkyne and solvent under reduced pressure, the residue was treated with lithium aluminium hydride in order to destroy the unchanged disulfide 1, which was thence totally converted into benzenethiol. Indeed, we found that elimination of the disulfide 1 greatly facilitated subsequent chromatographic separation of the desired benzothiophene product. Subsequent column chromatography on silica gel allowed isolation of the appropriate benzothiophenes 4a–i in varying yield along with small amounts of biphenyl 6. In the case of hex-1-yne 2h significant amounts of a mixture of the (*E*)- and (*Z*)-bis sulfide 5h were also isolated, whereas in the case of trimethylsilylacetylene 2g a little 1-(phenylthio)-1-trimethyl-silylprop-1-ene 8 was also obtained. The observed reaction products can be readily accounted for according to the reaction pathways outlined in Scheme 1. Methyl radicals, eventually produced from thermal fragmentation of TBP, would afford thioanisole and benzenethiyl radicals through an S_H2 reaction with diphenyl disulfide 1. Addition (reversible)[1,4] of the ensuing benzenethiyl radicals to the carbon–carbon triple bonds of the alkynes 2a–i would give the 2-(phenylthio)vinyl radicals 3a–i and thence the corresponding benzothiophenes 4a–i by a subsequent intramolecular cyclization. Trapping of the vinyl radical 3h by the disulfide 1 scavenger would give the bis sulfide 5h. The formation of some biphenyl 6 as well as diphenyl sulfide 7 (which could be generally detected by GLC) can be reasonably attributed to trapping of phenyl radical (probably resulting from S_H2 reaction of methyl radical with thioanisole) by the benzene solvent or the disulfide 1, respectively. As for the adduct 8, it arose possibly through reaction of the disulfide 1 with the 1-trimethylsilylpropenyl radical 9g, which might have been formed by addition of methyl radical to the alkyne 2g. As can be seen in Table 1, satisfactory yields of the benzo-thiophenes 4a–f could be generally obtained with the phenyl-acetylenes 2a–e and *tert*-butylacetylene 2f (entries 1–6, column A), whereas a low yield of the benzothiophene products 4h, i was obtained with hex-1-yne 2h and hex-3-yne 2i (entries 8 and 9, column A) in agreement with our previous results.[1] Tri-

methylsilylacetylene **2g** also led to a modest yield of the corresponding benzothiophene **4g**, at least under the above reaction conditions (entry 7, column A). An eight-fold increase in the concentration of the alkyne reactants **2a, c, f, h, i** did not bring about a concomitant increase in the yield of the resulting benzothiophenes **4a, c, f, h, i** (and the isomeric bis sulfides **5h**) [Table 1, entries 1, 3, 6, 8 and 9, column A (figures in brackets)]. Under these conditions the extent of thioanisole formation was generally found to be considerably reduced [Table 1, entries 1, 2, 6, 8 and 9, column A (figures in brackets)]. These findings might be explained by assuming that the alkynes **2a, c, f, g, i** would compete with diphenyl disulfide **1** for trapping of methyl radical.

In contrast to that observed with the alkynes **2a, c, f, h, i**, an eight-fold increase in the concentration of trimethylsilyl-acetylene **2g** resulted in a substantial enhancement of the yield of the benzothiophene **4g** (and the accompanying product **8**). The peculiar chemical trend observed with the alkyne **2g** is presumably ascribable to the fact that competing formation of the vinylic radical **9g** and its subsequent reaction with diphenyl disulfide **1** would not result in significant suppression of benzenethiyl radical (Scheme 1).
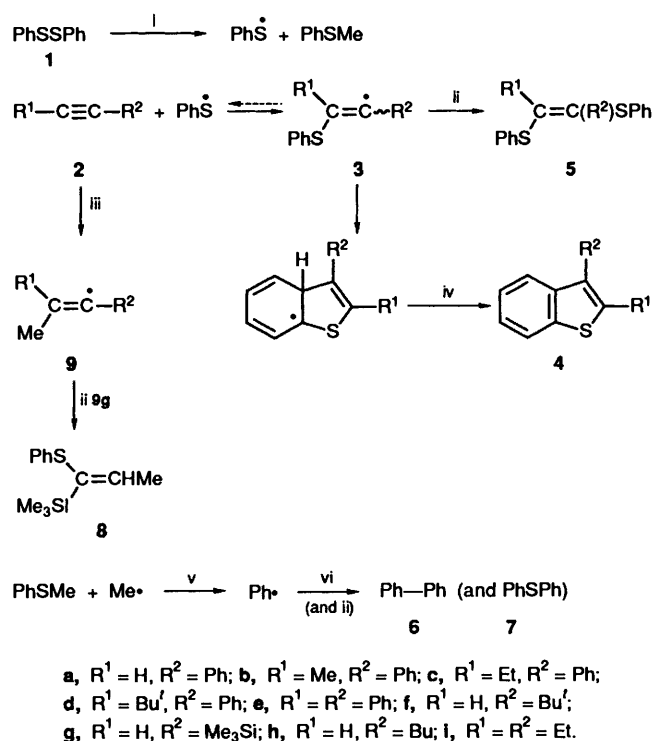

Scheme 1 *Reagents and conditions:* i, +TBP, 110 or 150 °C, benzene; ii, +1, −PhS·; iii, +Me·; iv, −H·; v, −Me$_2$S; vi, +benzene, −H·

The thermal reactions of the disulfide **1** with equimolar amounts of the alkynes **2a–c, f–h** in the presence of TBP, when carried out at 110 °C for 24 h, gave results comparable with those obtained from the corresponding reactions at 150 °C. However, the yields of the benzothiophene products **4a–c, f–h** were generally found to be somewhat lower (Table 1, entries 1–3, 6–9, column B); moreover, a 10-fold excess of TBP was generally required to achieve satisfactory conversion (*ca.* 90%) of the disulfide **1**. The observed yields of thioanisole (Table 1, entries 1–3, 6–9, column B) seem to suggest that under such thermal conditions the benzenethiyl radical is also mainly produced by an S$_H$2 reaction of methyl radical with diphenyl disulfide **1**. However, some additional intervention of initially formed *tert*-butoxy radical in promoting homolytic fission of diphenyl disulfide **1** might be suggested by the fact that with

the alkynes **2b** and **2f** significantly more of the benzothiophenes **4b** and **4f** were found than thioanisole. Radical attack of *tert*-butoxy radical at sulfur atom has been previously claimed to occur in the TBP-promoted decomposition of 1,2,3-benzothiadiazole at 110 °C.[5]

As observed with the corresponding reactions at 150 °C, an eight-fold increase in the concentration of the appropriate alkyne **2a–c, f–h**, whilst not substantially affecting the occurrence of the benzothiophene product **4a–c, h**, did cause a remarkable enhancement of the yield of the benzothiophenes **4g** and **4f** [Table 1, entries 1–3, 6–8, column B (figures in brackets)].

The thermal reactions of diphenyl disulfide **1** with the phenylacetylenes **2a, b** and the alkylacetylenes **2h–l** in the presence of dibenzoyl peroxide (DBP) were investigated in ethyl acetate at 100 °C for 3 h by using a five-fold excess of alkyne and a two-fold excess of the peroxide. These reactions, which generally led to rather complex product mixtures, were found to be synthetically unsatisfactory, but they were, however, rewarding since they provided evidence of possible addition of benzoyloxy radical to a carbon–carbon triple bond. Phenyl-acetylene **2a**, phenylpropyne **2b**, and hex-1-yne **2h** gave the desired benzothiophenes **4a, b, h** in isolated yields considerably lower than those provided by the corresponding reactions performed in the presence of TBP (Table 2, entries 2–4). Besides the benzothiophenes **4a, b, h** these unsymmetrical alkynes led also to *ca.* 1:1 isomeric mixtures of the (*E*)- and (*Z*)-2-(phenylthio)vinyl benzoate adducts **10a, h** and **10b** (exclusive of their regioisomers **11a, b, h**), which were found to occur to a major and minor extent, respectively (Table 2, entries 2–4). An isomeric mixture of the (*E*)- and (*Z*)-bis sulfide adduct **5h** was additionally obtained in 5% yield in the case of hex-1-yne **2h**, whereas in the case of phenylacetylene **2a** 2,4-diphenylthiophene was also obtained in 10% yield. The formation of this latter product was previously ascribed to addition of the vinylic radical **3a** to the alkyne **2a**, followed by intramolecular cyclization of the resulting vinyl radical.[1] The dialkylacetylenes **2i–l** furnished no benzothiophene product, but led to the (*E*)-vinylic adducts (*E*)-**10i–l** in 5–16% yield (Table 2, entries 5–8). Structural and configurational assignment of the previously unknown vinyl benzoates (*E*)-**10i–l** was based on their identity with authentic specimens obtained from BF$_3$-promoted reactions of 4′-nitrobenzenesulfenanilide (NBSA) with the alkynes **2i–l** in the presence of benzoic acid (Scheme 2). These last mentioned reactions are known to proceed with *trans*-stereospecificity through the intermediacy of thiirenium ions.[6] Structural and regiochemical assignments for the vinylic benzoates **10a, b, h** were established on the basis of ^{1}H NMR, MS and IR spectral data and by spectral comparison with authentic vinyl benzoates (*E*)-**11a, b, h** and (*E*)-**10h**, obtained
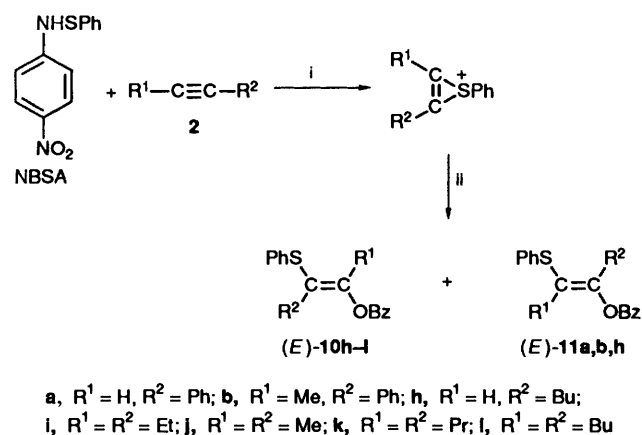

Scheme 2 *Reagents:* i, +BF$_3$·Et$_2$O, −ArNHBF$_3^-$; ii, +PhCO$_2$H, −H$^+$

from benzoyloxysulfenylation of the alkynes **2a, b, h** with NBSA in the presence of benzoic acid (Scheme 2). In agreement with our previous observation with related 2-(phenylthio)vinyl acetates,[6] the vinylic proton of the (*E*)-benzoates (*E*)-**11a, h** and the methylenic protons of the (*E*)-benzoate (*E*)-**11b** were found to occur at significantly higher field than the corresponding signals for (*E*)- and (*Z*)-**10a, h** and **10b**, respectively.

Control experiments ruled out the possibility that the adducts **10b** and **10h** might have resulted from isomerization of their possible initially formed regioisomers **11b** and **11h**, thus indicating that the compounds **10b, h** and, presumably, **10a** were actually produced under conditions of kinetic control. In fact, after a *ca.* 1:1 isomeric mixture of the (*E*)-adducts (*E*)-**10h** and (*E*)-**11h** in ethyl acetate had been heated at 100 °C for 2 h, in the presence of a five-fold excess of DBP and the disulfide **1**, subsequent column chromatography gave, in addition to un-identified material, a *ca.* 1:1 mixture of the unchanged compounds (*E*)-**10h** and (*E*)-**11h** together with a 1:1 mixture of their geometrical isomers (*Z*)-**10h** and (*Z*)-**11h** in *ca.* 2:1 ratio, respectively, and in *ca.* 20% overall yield. Under the same conditions the vinylic adduct (*E*)-**11b** was not isomerised, although substantial decomposition (*ca.* 80%) to unidentified products occurred. These experiments indicate that greater amounts of the benzoates **10a, b, h–l** are probably produced than yields of isolated material might suggest. Moreover, they also indicated that the observed stereochemistry of the benzoates **10a, b, h–l** does not necessarily reflect the actual stereochemical course of these benzoyloxysulfenylations, geometrical isomerization of the compounds under the reaction conditions being possible.

As can be seen in Table 2, the formation of diphenyl sulfide **7** (the product expected, in addition to benzenethiyl radical, from an S_H2 reaction of phenyl radical with diphenyl disulfide **1**) was found to decrease noticeably in the presence of the alkyne **2a, b, h, i** (Table 2, entries 1–5). Such an observation, in addition to the observed regiochemistry of the benzoyloxysulfenylation adducts **10a, b, h**, suggests that benzoyloxy radicals, initially produced from homolytic fragmentation of DBP, could be trapped by the alkynes **2a, b, h–l** and thus give the intermediate 2-(benzoyloxy)vinyl radicals **12a, b, h–l**. From these the final products **10a, b, h–l** could arise by further reaction with diphenyl disulfide **1** (Scheme 3).
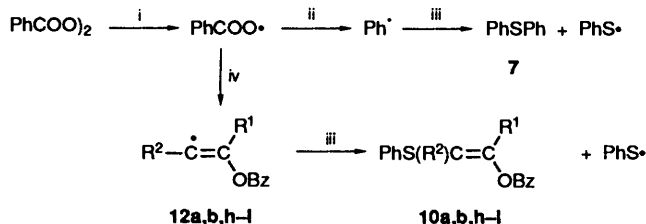
Scheme 3 *Reagents and conditions:* i, ethyl acetate, 100 °C; ii, -CO₂; iii, + **1**; iv, + **2a, b, h–l**

Kinetic studies were consistent with initial free-radical addition of benzoyloxy radical to the alkyne **2** in the observed (phenylthio)vinyl benzoate **10** formation. The thermal decomposition of 0.05 mol dm³ DBP in ethyl acetate at 100 °C was found to be cleanly first-order and quite unaffected by the presence of both the disulfide **1** (1 mol equiv.) and hex-3-yne **2i** (5 mol equiv.). These findings clearly ruled out the possible intervention of the disulfide **1** (or the alkyne **2i**) in the homolytic fragmentation of DBP. Evidence for thermal DBP decomposition promoted by sulfur compounds has been previously obtained.[7-9] A two-fold increase in the DBP concentration (0.1 mol dm³) was found to cause a significant enhancement of its decomposition rate; this was concomitantly found to follow no simple kinetic law. According to previous evidence,[10] at

such concentration the decomposition of DBP was probably assisted, at least in part, by the ensuing benzoyloxy and/or phenyl radicals. However, in the presence of both the disulfide **1** and the alkyne **2i**, the same reaction proved to be first-order, showing no rate enhancement. Under these circumstances, preferential trapping of benzoyloxy and phenyl radical by the alkyne **2i** and the disulfide **1** respectively would essentially prevent radical-induced decomposition of DBP.

In summary, we have shown that the thermal reaction of diphenyl disulfide **1** with simple alkynes at 100 and/or at 150 °C in the presence of di-*tert*-butyl peroxide can offer a useful one-pot method for the preparation of 3- (and 2,3-) substituted benzo[*b*]thiophenes, especially if phenylacetylenes or acetylenes bearing a bulky alkyl or silyl substituent are employed. On the other hand, analogous thermal reactions carried out in the presence of dibenzoyl peroxide proved to be of little synthetic utility, although they provided unprecedented examples of the free-radical addition of benzoyloxy radicals to carbon–carbon triple bonds. To our knowledge, the only reported instances of the free-radical addition of benzoyloxy radicals to unsaturated systems appear to be so far confined to those encountered in the thermal decomposition of DBP in the presence of furan[11] or anthracene,[12] eventually leading to the formation of 2,5-di(benzoyloxy)furan and 9-(benzoyloxy)-anthracene respectively.

Benzoyloxylation of anisole compounds has also been reported to occur in the thermal decomposition of DBP in the presence of such aromatic substrates. However, these substitutions probably proceed *via* initial electron transfer from aromatic substrate to benzoyloxy radical.[8]

Experimental

Diphenyl disulfide **1**, di-*tert*-butyl peroxide (TBP), dibenzoyl peroxide (DBP) and the alkynes **2a–c, e–l** were commercially available. The alkyne **2d**[13] and 4'-nitrobenzenesulfenanilide (NBSA)[14] were prepared according to the literature. The benzothiophenes **4a,**[2e] **4b,**[15] **4d,**[1] **4e,**[16] **4f,**[2b] **4h**[2e] and **4i**[2c] were each identified by comparison of their ¹H NMR spectra with those reported in literature as well as by mass spectral (MS) analysis. The bis sulfides **5a, h,**[17] 2,4-diphenylthiophene,[18] biphenyl **6**, diphenyl sulfide **7** and benzoic acid were identified by comparison (GLC, GLC–MS) with authentic specimens. The homogeneity of the hitherto unknown benzothiophenes **4c, g** and vinyl benzoates (*E*)-**10i–l** and (*E*)-**11a, b** was confirmed by TLC and GLC–MS analysis.

¹H NMR spectra were measured on a Varian Gemini 200 (200 MHz) instrument, and are for CDCl₃ solutions with SiMe₄ as internal standard; *J* values are in Hz. IR spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrophotometer. Mass spectra were determined by the electron impact method on a VG 7070 instrument. GLC–MS analyses were performed on a GC/MS workstation HP 59970. GLC analyses were performed on a Varian 3700 instrument, equipped with a FID detector, using a 3% SE30 column. HPLC analyses were performed on a Varian LC 5000 instrument using a C-18 column. Column chromatography was carried out on Merck Silica gel (0.040–0.063 particle size).

Thermal Reactions of Diphenyl Disulfide **1** *with Alkynes* **2** *Promoted by Di-*tert-*butyl Peroxide (TBP).—Procedure A.* A solution of the disulfide **1** (436 mg, 2 mmol), TBP (0.73 cm³, 4 mmol) and the appropriate alkyne **2a–i** (2 mmol) in benzene (20 cm³) was heated in a sealed tube at 150 °C for 3 h, after which time the resulting reaction mixture was directly assayed by GLC for the amount of unchanged disulfide **1** and thio-anisole produced (yields are given in Table 1). Subsequently, the excess of solvent, the unchanged alkyne **2a–d, f–i** and thioanisole were evaporated off under reduced pressure. The

Table 1 Yields (%) of benzo[b]thiophenes **4** and thioanisole obtained from the di-tert-butyl peroxide-promoted reaction of diphenyl disulfide **1** with equimolar amounts of the alkyne **2** at 150 °C (A) and 110 °C (B)

		Benzothiophene		PhSMe	
Entry	Alkyne	A[a,b]	B[c,b]	A[c,b]	B[c,b]
1	Phenylacetylene **2a**	**4a**, 44 [43]	25 [31]	53 [20]	54 [30]
2	1-Phenylpropyne **2b**	**4b**, 75	73 [67]	75	50 [43]
3	1-Phenylbut-1-yne **2c**	**4c**, 54 [38]	44 [46]	73 [42]	58 [55]
4	Phenyl-tert-butylacetylene **2d**	**4d**, 44		—	
5	Diphenylacetylene **2e**[d]	**4e**, 60		120	
6	tert-Butylacetylene **2f**	**4f**, 67 [73]	65 [92]	78 [50]	50 [39]
7	Trimethylsilylacetylene **2g**[d]	**4g**, 22 [60]	6 [47]	64 [35]	53 [31]
8	Hex-1-yne **2h**[e]	**4h**, 18 [16]	18 [16]	50 [23]	45 [31]
9	Hex-3-yne **2i**	**4i**, 10 [14]		70 [38]	

[a] Yields isolated by column chromatography and based on reacted disulfide **1** (85–90%). Biphenyl **6** (2–3%) was also generally isolated. GLC showed general occurrence of diphenyl sulfide **7** (ca. 1–2%). [b] Yields in brackets were determined by GLC for reactions carried out by using a ca. eight-fold excess of the appropriate alkyne **2**. [c] Yields calculated by GLC and based on reacted disulfide **1**. [d] 1-(Phenylthio)-1-trimethylsilylpropene **8** was also obtained in 4 [20] (A) and 3 [8]% (B) yield respectively. [e] An unresolved mixture of the (E)- and (Z)-bis sulfide **5** was also obtained in 15 [16] (A) and 17 [12]% (B) yield respectively.

residue was dissolved in anhydrous diethyl ether (30 cm³) and treated with lithium aluminium hydride for a few minutes, after which the mixture was hydrolysed with water. The organic layer was separated and evaporated and the residue chromatographed. Elution with light petroleum (b.p. 40–70 °C) furnished (as appropriate) (i) unchanged **2e** (37%); (ii) biphenyl **6** (2–3%); (iii) the appropriate benzothiophene **4a–i**; (iv) an unresolved mixture of the (E)- and (Z)-bis sulfide **5h** (15%); and (v) little amounts of unidentified products. The isolated benzothiophene **4g** was found to be contaminated with some 1-phenylthio-1-trimethylsilylpropane **8**. Repeated column chromatography allowed separation of the pure benzothiophene **4g** and the propene **8** contaminated with small amounts of **4g**; δ_H 0.05 (9 H, s), 1.90 (3 H, d, J 6), 6.70 (1 H, q, J 7) and 7.15–7.40 (5 H, m); m/z 222 (M⁺), 207, 167 (100), 151, 117, 91, 73 (100) and 45.

Yields of the benzothiophenes **4a–i** are given in Table 1, column A. The following two new benzothiophenes were obtained as oily products: (i) 2-ethyl-3-phenylbenzo[b]thiophene **4c**, δ_H 1.22 (3 H, t, J 7.5), 2.80 (2 H, q, J 7.5) and 7.0–7.8 (9 H, m) (Found: M⁺, 238.0825. C₁₆H₁₄S requires M, 238.0816); m/z 238 (100), 223, 178, 128 and 111; and (ii) 3-trimethylsilyl-benzo[b]thiophene **4g**, δ_H 0.40 (9 H, s), 7.3–7.4 (2 H, m), 7.53 (1 H, s) and 7.9–8.0 (2 H, m) (Found: M⁺, 206.0825. C₁₁H₁₄SSi requires M, 238.0816); m/z 206, 191 (100), 115, 101 and 96.

The above reactions were similarly repeated by using a solution of the disulfide **1** (218 mg, 1 mmol) and TBP (0.37 cm³, 2 mmol) in benzene (10 cm³) containing the appropriate alkyne **2a, c, f–i** (8 mmol). The resulting reaction mixture was directly analysed by GLC and GLC–MS. Yields of the benzothiophenes **4a, c, g–i** and thioanisole are reported in Table 1, columns A (figure in brackets).

Procedure B. A solution of the disulfide **1** (218 mg, 1 mmol), TBP (1.8 cm³, 10 mmol) and the appropriate alkyne **2a–c, f–h** (1 mmol) in benzene (10 cm³) was heated at 110 °C for 24 h in a sealed tube. After this time the resulting reaction mixture was directly analysed by GLC and GLC–MS. Yields of the benzothiophenes **4a–c, f–h** and thioanisole are given in Table 1, columns B, and were based on disulfide **1** which had reacted (90–95%). The above reactions were similarly repeated by using a solution of the disulfide **1** (1 mmol) and TBP (10 mmol) in benzene (10 cm³) containing the appropriate alkyne **2a–c, f–h** (8 mmol). The resulting reaction mixtures was directly analysed by GLC and GLC–MS. Yields of the benzothiophenes **4a–c, f–h** and thioanisole are reported in Table 1, columns B (figures in brackets).

*Thermal Reactions of Diphenyl Disulfide **1** with Alkynes **2** Promoted by Dibenzoyl Peroxide (DBP): General Procedure.—*

A solution of diphenyl disulfide **1** (436 mg, 2 mmol), DBP (484 mg, 4 mmol) and the appropriate alkyne **2a, b, h–l** (10 mmol) in ethyl acetate (20 mmol) was heated in a sealed tube at 100 °C for 3 h. After this time the excess of solvent and alkyne was removed under reduced pressure and the residue chromatographed. Gradual elution with light petroleum (b.p. 40–70 °C)–diethyl ether mixtures (up to 50% diethyl ether) furnished (as appropriate): (i) unchanged disulfide **1** (30–40%); (ii) the appropriate benzothiophene **4a, b, h**; (iii) diphenyl sulfide **7**; (iv) an unresolved mixture of the (E)- and (Z)- bis sulfide **5a** (3%) or **5h** (5%); (v) the appropriate vinyl benzoate (E)-**10i–l** and unresolved mixtures of the (E)- and (Z)-vinyl benzoates **10a, b, h**; (vi) benzoic acid (30–40%); and (vii) tarry material (ca. 200 mg). In the case of phenylacetylene **2a** chromatography also gave 2,4-diphenylthiophene in 10% yield. Yields of the isolated sulfide **7**, the benzothiophenes **4a, b, h**, and the vinylic adducts **10a, b, h–l** are given in Table 2.

The new isolated (E)-adducts (E)-**10i–l** were identical in all respects (GLC, ¹H NMR and MS) with authentic specimens independently prepared (vide infra).

1-Benzoyloxy-2-(phenylthio)hex-1-ene **10h**. This compound was obtained as an inseparable ca. 1:1 mixture of (E)- and (Z)-isomers; ν_{max}/cm⁻¹ 1730, 1259 and 1245 (Found: 73.3; H, 6.6; S, 10.15. C₁₉H₂₀O₂S requires C, 73.05; H, 6.45; S, 10.25%); the (E)-isomer was identical in all respects (¹H NMR, GLC, GLC–MS) with an authentic specimen independently prepared (see later); the (Z)-isomer had δ_H 0.9 (3 H, t, J 7.5), 1.2–1.7 (4 H, m), 2.20 (2 H, t, J 7.5), 7.1–7.7 (9 H, m), and 8.0 (2 H, d, J 8); GLC–MS spectrum: m/z 312 (M⁺), 203, 105 (100) and 77.

β-Benzoyloxy-α-(phenylthio)styrene **10a**. This compound was obtained as an inseparable ca. 1:1 mixture of (E)- and (Z)-isomers; δ_H 7.0–7.8 (26 H, m), 8.07 (4 H, m), 8.18 (1 H, s) and 8.25 (1 H, s); the two isomers had identical GLC–MS spectra: m/z 332 (M⁺), 210, 165, 121, 105 (100) and 77; ν_{max}/cm⁻¹ 1741, 1259 and 1244 (Found: C, 76.2; H, 4.95; S, 9.75. C₂₁H₁₆O₂S requires C, 75.9; H, 4.85; S, 9.65%).

β-Benzoyloxy-β-methyl-α-(phenylthio)styrene **10b**. This compound was obtained as a ca. 1:1 mixture of (E)- and (Z)-isomers contaminated with minor amounts of inseparable, unidentified products; δ_H 2.15 (3 H, s), 2.50 (3 H, s), 7.0–7.6 (m), 7.9 (2 H, m) and 8.1–8.2 (2 H, m); the two isomers had identical GLC–MS spectra: m/z 346 (M⁺), 237, 163, 132, 121, 105 (100) and 77.

Thermolysis of the Vinyl Benzoates (E)-**10h**, (E)-**11h** *and* (E)-**11b** *in the Presence of Diphenyl Disulfide **1** and DBP.—*A ca. 1:1 mixture of (E)-1-benzoyloxy-2-(phenylthio)hex-1-ene (E)-**10h** and (E)-2-benzoyloxy-1-(phenylthio)hex-1-ene (E)-**11h** (60 mg, 0.2 mmol) in ethyl acetate containing DBP (240 mg,

Table 2 Products yields[a] (%) for the dibenzoyl peroxide-promoted reaction of diphenyl disulfide 1 with alkynes 2 at 100 °C[b]

Entry	Alkyne	Diphenyl sulfide 7	Vinyl benzoate	Benzothiophene
1	None	75		
2	Phenylacetylene 2a[c,e]	18	10a,[d] 19	4a, 15
3	Phenylpropyne 2b	21	10b,[d] 3	4b, 49
4	Hex-1-yne 2h[e]	28	10h,[d] 19	4h, 9
5	Hex-3-yne 2i	45	(E)-10i, 16	None
6	But-2-yne 2j	f	(E)-10j, 15	None
7	Oct-4-yne 2k	f	(E)-10k, 6	None
8	Dec-5-yne 2l	f	(E)-10l, 5	None

[a] Yields isolated by column chromatography and based on reacted disulfide 1 (60–70%).[b] Benzoic acid and noticeable amounts of tarry products were also generally obtained. [c] 2,4-Diphenylthiophene was also obtained in *ca.* 10% yield. [d] *ca.* 1:1 Mixture of (E)- and (Z)-isomer. [e] An unresolved mixture of the corresponding (E)- and (Z)-bis sulfide 5 was also obtained in *ca.* 3–5% yield. [f] Yield not determined.

1 mmol) and the disulfide 1 (218 mg, 1 mmol) was heated in a sealed tube at 100 °C for 2 h, after which time the solvent was removed and the residue chromatographed. Elution with a 90:10 mixture of light petroleum (b.p. 40–70 °C) and diethyl ether gave (i) a mixture (12 mg, 20%) of the vinyl benzoates (E)-10h, (Z)-10h, (E)-11h, and (probably) (Z)-11h in a *ca.* 2:1:2:1 ratio, as indicated by ^{1}H NMR spectroscopy, GLC–MS and GLC. The ^{1}H NMR spectrum showed, in addition to the vinylic methylene groups and the vinylic protons of the benzoates (E)-10h, (E)-11h and (Z)-10h, signals at δ 2.47 (2 H, t) and 5.95 (1 H, s) ascribable to the vinylic methylenic group and the vinylic proton of (Z)-11h; and (ii) unidentified products.

(E)-α-Benzoyloxy-β-methyl-β-(phenylthio)styrene (E)-11b (35 mg, 0.1 mmol) was similarly allowed to react in ethyl acetate (5 cm³) in the presence of DBP (120 mg, 0.5 mmol) and the disulfide 1 (110 mg, 0.5 mmol). GLC–MS analysis of the resulting reaction mixture established the absence of any isomeric vinyl benzoate. Subsequent column chromatography gave (i) unchanged (E)-11b (7 mg, 20% recovery) and (ii) a number of unidentified products.

Synthesis of the Vinyl Benzoates (E)-10h–l *and* (E)-11a, b, h: *General Procedure.*—To a stirred solution of 4′-nitrobenzene-sulfenanilide (NBSA) (246 mg, 1 mmol), benzoic acid (1.2 g, 10 mmol) and the appropriate alkyne 2a, b, h–l (10 mmol) in benzene (10 cm³) boron trifluoride–diethyl ether complex (*ca.* 47% BF₃; 0.19 cm³, 1.5 mmol) was added at room temperature. The reaction mixture was stirred at room temperature for 1 h and then neutralized with 10% aqueous sodium carbonate. The organic layer was extracted with diethyl ether and the extract was evaporated to afford a residue; this was then chromatographed. Gradual elution with light petroleum (b.p. 40–70 °C)–diethyl ether mixtures gave (i) variable amounts of the disulfide 1 and (ii) the appropriate vinyl benzoate(s) (E)-10h–l and/or (E)-11a, b, h. These compounds were generally found to undergo significant decomposition during chromatographic work-up, to give unidentified products. Further elution gave (iii) unidentified material; (iv) unchanged benzoic acid; and (v) 4-nitroaniline. The following new (E)-vinyl benzoates (E)-10 and (E)-11 were obtained as oily products (yield in parentheses): (i) (E)-α-benzoyloxy-β-(phenylthio)styrene (E)-11a (8%), δ_H 6.45 (1 H, s), 7.2–7.7 (13 H, m) and 8.18 (2 H, d, *J* 8) (Found: M⁺, 332.0880. C₂₁H₁₆O₂S requires *M*, 332.0871); *m/z* 332, 223, 105 (100) and 77; ν_max/cm⁻¹ 1735, 1257 and 1084; (ii) (E)-α-benzoyloxy-β-methyl-β-(phenylthio)styrene (E)-11b (17%), δ_H 2.02 (3 H, s), 7.1–7.7 (13 H, m) and 8.0–8.2 (2 H, m) (Found: M⁺, 346.1035. C₂₂H₁₈O₂S requires *M*, 346.1027); *m/z* 346, 237, 135, 105 (100) and 77; ν_max/cm⁻¹ 1742, 1372 and 1240; (iii) an unresolved 1:1.3 mixture (23%) of (E)-1-benzoyloxy-(2-(phenylthio)hex-1-ene (E)-10h, δ_H 0.88 (3 H, t, *J* 7.5), 1.2–1.7 (4 H, m), 2.42 (2 H, t, *J* 7), 7.1–7.7 (8 H, m), 7.80 (1 H, s), and 8.1 (2 H, d, *J* 8); *m/z* (GLC–MS) 312 (M⁺), 203, 105 (100) and 77;

and (E)-2-benzoyloxy-1-(phenylthio)hex-1-ene (E)-11h; δ_H 0.9 (3 H, t, *J* 7.5), 1.2–1.7 (4 H, m), 2.65 (2 H, t, *J* 7), 6.10 (1 H, s), 7.1–7.7 (8 H, m) and 8.1 (2 H, d, *J* 8); *m/z* (GLC–MS) 312 (M⁺), 228, 105 (100) and 77; ν_max/cm⁻¹ 1730 and 1260 (Found: C, 73.1; H, 6.55; S, 10.1. C₁₉H₂₀O₂S requires C, 73.05; H, 6.45; S, 10.25%); (iv) (E)-3-benzoyloxy-4-(phenylthio)hex-3-ene (E)-10i (26%); δ_H 1.00 (3 H, t, *J* 7.5), 1.08 (3 H, t, *J* 7.5), 2.18 (2 H, q, *J* 7.5), 2.78 (2 H, q, *J* 7.5), 7.1–7.77 (8 H, m) and 8.17 (2 H, d, *J* 8) (Found: M⁺, 312.1192. C₁₉H₂₀O₂S requires *M*, 312.1184); *m/z* 312, 203, 105 (100) and 77; ν_max/cm⁻¹ 1725, 1259 and 1174, (v) (E)-2-benzoyloxy-3-(phenylthio)but-2-ene (E)-10j (30%); δ_H 1.87 (3 H, q, *J* 1.5), 2.32 (3 H, q, *J* 1.5), 7.2–7.8 (8 H, m) and 8.1–8.3 (2 H, m) (Found: M⁺, 284.0864. C₁₇H₁₆O₂S requires *M*, 284.0871); *m/z* 284, 175, 105 (100) and 77; ν_max/cm⁻¹ 1724, 1270 and 1228; (vi) (E)-4-benzoyloxy-5-(phenylthio)oct-4-ene (E)-10k (50%); δ_H 0.82 (3 H, t, *J* 7.5), 0.96 (3 H, t, *J* 7.5), 1.4–1.65 (4 H, m), 2.17 (2 H, t, *J* 7.5), 2.79 (2 H, t, *J* 7.5), 7.1–7.7 (8 H, m) and 8.16 (2 H, d, *J* 8) (Found: M⁺, 340.1508. C₂₁H₂₄O₂S requires *M*, 340.1497); *m/z* 340, 231, 105 (100) and 77; ν_max/cm⁻¹ 1728, 1272 and 1172; and (vii) (E)-5-benzoyloxy-6-(phenylthio)dec-5-ene (E)-10l (56%); δ_H 0.77 (3 H, t, *J* 7), 0.88 (3 H, t, *J* 7), 1.1–1.6 (8 H, m), 2.17 (2 H, t, *J* 7), 2.79 (2 H, t, *J* 7), 7.1–7.7 (8 H, m) and 8.15 (2 H, d, *J* 8) (Found: M⁺, 368.1816. C₂₃H₂₈O₂S requires *M*, 368.1810); *m/z* 368, 258, 105 (100) and 77; ν_max/cm⁻¹ 1724, 1271 and 1228.

Kinetic Measurements.—Kinetic measurements of the thermal decomposition of DBP in ethyl acetate at 100 °C were performed at DBP concentrations 0.05 and 0.1 mol dm⁻³ both in the absence [(A) and (B) respectively] and in the presence of diphenyl disulfide 1 (1 mol equiv.) and aikyne 2i (5 mol equiv.) [(C) and (D) respectively]. In each case, the appropriate reaction mixture was partitioned in sealed tubes, which were kept in a oil-bath at 100 °C. The tubes were removed at regular intervals, suitably diluted with acetonitrile and assayed by HPLC on a C-18 column with acetonitrile as eluent. The first tube was removed after 5 min and taken as zero point. In the cases (A), (C) and (D) the decomposition of DBP was cleanly first-order and the observed rate constant was *K* = 1.3 · 10⁻², 1.35 · 10⁻² and 1.45 · 10⁻² min⁻¹ respectively. In the case (B) the decomposition of DBP followed no simple kinetic law; the observed half life times were as follows: first *t*₁ = 12 min, second *t*₁ = third *t*₁ = 22 min.

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